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# Title: Formation of soluble mercury oxide coatings: transformation of elemental mercury in soils

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**Abstract**

The impact of mercury (Hg) on human and ecological health has been known for decades. Although a treaty signed in 2013 by 147 nations regulates future large-scale mercury emissions, legacy Hg contamination exists worldwide and small scale releases will continue. The fate of elemental mercury, Hg(0), lost to the subsurface and its potential chemical transformation that can lead to changes in speciation and mobility are poorly understood. Here we show that Hg(0) beads interact with soil or manganese oxide solids and x-ray spectroscopic analysis indicates that the soluble mercury coatings are HgO. Dissolution studies show that after reacting with a composite soil, > 20 times more Hg is released into water from the coated beads than from a pure liquid mercury bead. An even larger, > 700 times, release occurs from coated Hg(0) beads that have been reacted with manganese oxide, suggesting that manganese oxides are involved in the transformation of the Hg(0) beads and creation of the soluble mercury coatings. Although the coatings may inhibit Hg(0) evaporation, the high solubility of the coatings can enhance Hg(II) migration away from the Hg(0)-spill site and result in potential changes in mercury speciation in the soil and increased mercury mobility.

## Introduction

More than 3000 mercury (Hg) contaminated sites exist worldwide due to the use of elemental Hg in industrial processes (chlor-alkali plants, artisanal and precious metal mining) and the conversion of mercury ore to elemental mercury in thermal processes (Hg mining and non-ferrous metal production). These Hg processing sites often contain soils contaminated with liquid elemental mercury ($Hg(0)_l$).[1] Although a treaty signed in 2013 by 147 nations regulates future large-scale mercury emissions, legacy mercury contamination and small scale releases will continue to impact the environment.[2] Localized spills of $Hg(0)_l$ can result in highly contaminated soils that are sources of Hg to the atmosphere and aquatic systems. The fate of elemental mercury lost to the subsurface and the potential for mercury release into groundwater and surface water remain poorly understood.

The speciation of Hg is dependent on both the source of Hg and the environment in which the Hg is deposited. The dominant Hg species in low level or uncontaminated soils include highly insoluble Hg-sulfide compounds such as metacinnabar (solubility = $10^{-23.7}$ M) and potentially mobile Hg-organic complexes.[3,4]

Several methods, including sequential extractions, thermal analysis, and Extended X-ray Absorption Fine Structure (EXAFS)[5-13] have been used to examine Hg speciation in Hg contaminated soils. Hg has been shown to be present in the form of $Hg(0)_l$, in addition to oxidized forms (e.g., Hg(II)) associated with organics or mineral phases or as metacinnabar in contaminated sites.[5-13] In a study conducted with soils from the Amazon incubated with Hg(0), it was determined using Hg thermal desorption methods, that 26-68% of the Hg(0) was converted to Hg(II).[14] Similarly using Hg thermal desorption analysis, 70-100% of the Hg adsorbed onto

platelets of various soil types and horizons were determined to have been transformed to oxidized Hg(II) after being saturated with Hg(0) vapors.[15] Although Hg-organic complexes typically dominate the speciation of mercury[4, 12] in uncontaminated soils, studies of soil contaminated with $Hg(0)_l$ have shown that Hg-sulfide species, such as metacinnabar, are more common[3, 8, 13, 7]. For example, at a site contaminated with $Hg(0)_l$ in Oak Ridge, TN, Hg in soils collected just below an accumulation of $Hg(0)_l$ was dominated by Hg-sulfide complexes. However, soil samples from the same site, which contained no $Hg(0)_l$ and had low Hg levels similar to uncontaminated sites, showed that the Hg was mostly present as Hg-organic complexes[7]. Hg-sulfide was also found in soils surrounding chlor-alkali facilities, where $Hg(0)_l$ spills occurred[3,13]. The difference in Hg speciation in soils with and without $Hg(0)_l$ sources highlights the need to understand the chemical transformation of $Hg(0)_l$ in soils since these transformations will influence the mobility and speciation at Hg contaminated sites. Understanding these transformations is a critical step toward developing models to predict the movement of Hg at contaminated sites.

In a previous study we observed that $Hg(0)_l$ beads collected from contaminated Y-12 soils had a dull coatings on them[7]. In this study, we more closely examine the coatings on $Hg(0)_l$ beads that were removed from these soils. Laboratory experiments were conducted to examine changes in Hg speciation at the surface of $Hg(0)_l$ as a result of interaction with soils and pure mineral phases. We attempted to resolve the speciation of Hg on the surfaces of $Hg(0)_l$ beads using scanning electron microscopy. Changes in the solubility of mercury were evaluated in laboratory experiments using $Hg(0)_l$ before and after its interaction with soils and mineral phases. Collectively, the study aimed to examine transformation of the $Hg(0)_l$.

## Experimental

*Soil collection*

Soil cores containing visible beads of liquid Hg were collected from the vadose zone in May 2011 from the Y-12 National Security Complex (Y-12) in areas with >1000 mg/kg Hg.[7] A dual-tube coring system was used to obtain cores to a depth of ~4.0 m. Soil and sediment were sampled from the cores at ~7.5-cm intervals and stored at 4º C until analysis.[7] $Hg(0)_l$ beads were carefully removed from the soil samples for laboratory experiments and SEM imaging, using a spatula to minimize any disturbance of the bead surfaces. An uncontaminated composite soil sample was prepared by combining soils from several locations at the Y-12 facility for use in laboratory experiments. Based on headspace analysis, these soil samples were found to be absent of Hg(0) vapors, so it was assumed they did not contain any $Hg(0)_l$. After combining the soils, the composite was sieved through 2mm-sieve and homogenized by hand-mixing. The resultant composite had a total Hg concentration of 0.03 mg/kg. The concentration of other metals (Supporting Information Fig. S2) was determined, using an acid digestion followed by detection by inductively coupled plasma-mass spectrometry (EPA method 3050) for this composite sample.

*Imaging*

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out using a Zeiss Merlin SEM equipped with a Bruker solid-state EDS detector and state-of-the-art in-lens detectors which enables high-resolution secondary imaging using low-energy electron beams. For SEM analysis, mercury beads were transferred to conductive carbon tape using tweezers. For large beads only a small portion of the bead and coating were extracted and used for analysis to minimize the amount of Hg(0) introduced into the SEM, since Hg(0)

vapors can amalgamate with parts of the SEM. A standard HgO powder obtained from Sigma Aldrich was used in SEM and EDS analysis for verification. The reagent grade Mn and Fe media used in the laboratory experiments were characterized by X-ray diffraction using a Panalytical Xpert diffractometer and X'Celerator detector. A search match was conducted using "Jade" (Materials Data, Inc.) and/or HighScore (PANalytical) software and the International Centre for diffraction data (ICDD) database to identify the solids. Details on the methods used for the SEM and EDS measurements are described in the Supporting Materials.

*Coating development on $Hg(0)_l$*

Beads of $Hg(0)_l$ were exposed to a range of media (Table 1) to examine factors controlling the formation of the coating on the bead surface under controlled experimental conditions. For laboratory experiments $Hg(0)_l$ (Fisher, Laboratory grade) was washed with nitric acid (1.4 M) followed by three rinses with deionized water (18.2 megohm). Washed $Hg(0)_l$ was stored in a vial containing deoxygenated water with a $N_2$ gas filled headspace as a 'stock $Hg(0)_l$'. For dissolution experiments small beads of washed $Hg(0)_l$ (50 µl) were removed from the stock container using a gas tight syringe in a $N_2$ gas filled glove bag and placed in 5 ml glass vials. The solid phase media was added to the vial so that the bead was completely covered by the fine granular solid being tested. The beads of $Hg(0)_l$ were allowed to react in the dark, without agitation, with the solid for 8-157 days. At the end of the treatment, beads were recovered using a spatula and placed in 40 mL amber glass vials for aqueous dissolution studies (see next section). Laboratory tests were conducted under oxic ambient atmospheric conditions unless noted. Control experiments, using the pure stock $Hg(0)_l$, were performed and used as a baseline to compare to all other treatments. Solid media, including $Fe_2O_3$, $MnO_2$ and $Mn_2O_3$, clay and

quartz were characterized before use (see Supporting Information). For all experiments, except when noted, the solids were used as received – no attempt was made to remove moisture. To determine the effect of free water on $Hg(0)_l$ transformation by solid media, oven dried (105$^oC$) $Mn_2O_3$ samples were used and results were compared to the other treatments. After oven drying, the $Mn_2O_3$ sample was held in a $N_2$ flushed glove bag containing a calcium sulfate desiccant.

The presence of oxidized Hg associated with the $Hg(0)_l$ beads was determined by measuring the dissolved Hg(II) after the addition of water to the bead. Deionized water was added to the glass vial containing treated beads and the vial was immediately capped. The vial cap was fitted with an outlet port consisting of Teflon tube (1.6 mm internal diameter) secured approximately 10 mm from the base of the vial (Supporting Information Fig. S3). Aqueous samples (1 ml) were withdrawn from the vial with a plastic syringe following a 0.5 mL flush of the sample line. A sub-sample was immediately analyzed for dissolved $Hg(0)_{aq}$ and the remaining aliquot was preserved with bromine monochloride (BrCl) for total mercury analysis. A 20 ml syringe filled with air was used to equilibrate the headspace of the vial as the liquid sample was removed. The contents in the glass vials were gently mixed using a rotating table (160 rpm) during the course of the experiment. The concentrations of dissolved $Hg(0)_{aq}$ and total Hg were measured multiple times between 10 and 300 minutes using a modification [7] of EPA method 1631E. For $Hg(0)_{aq}$ measurements, the Hg(0) was purged from the sample (50 µl sample added to ~ 10 mL of mercury free water) and detected using cold vapor atomic absorption spectroscopy (CVAAS; RA-915+Hg, Ohio Lumex). For total Hg analysis, the samples were treated with BrCl for a minimum of 24 hours to oxidize the Hg(0) and organic matter in the sample. Stannous chloride was added to the sample and the resulting Hg(0) was purged and detected using CVAAS. Analytical detection limits were calculated daily and the

values were always below 100 pg. All samples, with the exception of the blanks, were above this detection limit. The average standard deviation between duplicate HgT measurements were 1.5% and the average recovery of routinely analyzed reference materials (IAEA433, NIST 8407 and CRM 580) was 98(+/-3)%. Analytical blanks and procedural blanks, which quantified the Hg associated with the experimental containers, were below detection limits. The concentration of Hg(II) was determined as the difference between the total Hg and dissolved Hg(0) concentration. Concentrations of Hg(II) released from the beads were normalized to the bead surface area, determined from the bead volume or weight and the density of mercury, assuming a spherical bead. This normalization was conducted to adjust for the different sizes of beads removed from Hg(0) contaminated soils.

## Results and Discussion

*Hg coatings on $Hg(0)_l$ beads*

Transformations of $Hg(0)_l$ in soils were examined by using samples collected at the Y-12 facility, which are contaminated due to $Hg(0)_l$ use and multiple spills between 1950-1963[7, 16]. Mercury beads from the mercury spill site are clearly shown in photograph (Fig. 1a) ranging from microscopic to mm sizes. Compared to a clean, pure $Hg(0)_l$ (Fig. 1b), a dull coating is clearly seen on beads in the soils. Closer examination with SEM (Fig. 1e) of a $Hg(0)_l$ bead from the contaminated soil shows a distinct solid phase coating. The dull coatings were also observed with $Hg(0)_l$ beads that had been reacted with soils in the laboratory (Fig. 1 c,d). Microstructural analysis of $Hg(0)_l$ of a bead extracted from the Y-12 soil cores revealed ubiquitous clusters of crystals on the surface (Fig. 2a-b). Comparing EDS analyses of crystals on the exterior of the bead and the $Hg(0)_l$ on the interior of the bead indicates that the crystalline solid is a mercury

oxide (Fig. 2c). EDS spectra (Fig. 2d) collected from both a solid crystal and liquid interior spot of the bead (Fig. 2c) show that both regions contain a peak at approximately 2.2 keV, which is indicative of the Hg. However, the EDS spectrum of the solid crystal also contains a strong peak at 0.5 keV, corresponding to the presence of oxygen in the structure of the crystals, which agreed well with the EDS spectra of the standard HgO (Supporting Information Fig. S4b). The crystals in the SEM images (Fig 2a-c) have an orthorhombic structure that also resembles the structure of the HgO montroydite (Supporting Information Fig. S4a). The crystals from this sample ranged from 10 to 1000 nm in size. Clay particles were also observed on the surface of the beads (Fig. 2a).

Laboratory experiments demonstrate that when placed in deionized water, $Hg(0)_l$ beads extracted from the Y-12 soils [in-situ $Hg(0)_l$] release oxidized Hg at concentrations 15-45 times greater than pure beads of $Hg(0)_l$ (Fig. 3). The oxidized Hg is in either the +1 or +2 valance state; hereafter, Hg(II) is used to signify both Hg oxidation states because the analytical methods do not distinguish between the two and Hg(II) is the inorganic mercury form typically found in the environment. For pure, stock $Hg(0)_l$ beads, the amount of Hg(II) released, based on bead surface area, at initial (~10 minutes) and final (300 minutes) time points, was 1.7 (±0.9) and 7.6 (±4.0) nmol/m$^2$, respectively. This gradual increase over time is in part due to the oxidation of dissolved gaseous mercury ($Hg(0)_d$) and is consistent with other studies[17]. Two $Hg(0)_l$ beads from contaminated soil (with mass of 0.974 g and 0.588g) respectively released Hg(II) at 61.4 nmol/m$^2$ and 30.8 nmol/m$^2$ within the first 10 minutes, under the same experimental conditions used for the pure $Hg(0)_l$ beads (Fig. 3). Such rapid release of Hg(II) suggests that oxidized Hg species are present on the surface of the $Hg(0)_l$ beads collected from *in situ* soils and are rapidly dissolved in water (Supporting Information Fig. S1, Discussion 1). This is consistent with the

spectroscopic characterization where SEM and EDS suggested the presence of HgO on the surface of $Hg(0)_l$ beads associated with contaminated site soil.

*Oxidation of $Hg(0)_l$ by solid phase media*

Subsequent laboratory experiments were conducted to determine which commom mineral assemblages found in soil result in the same oxidization of Hg, and formation of coatings on the surface of $Hg(0)_l$ beads, that is observed in Y-12 soils. To varying degrees we observed the oxidation of the Hg(0) and coating formation using pure $Hg(0)_l$ beads, covered by an uncontaminated soil composite from Y-12 and a few other solid media, including Fe and Mn oxides, kaolinite, and silica sand (Table 1, Fig. 4). In this set of experiments, pure stock $Hg(0)_l$ beads were reacted with various solid phases for set time periods in an ambient laboratory atmosphere. Ambient laboratory air was routinely measured and the Hg concentrations were below detection limits. After reaction periods, the beads were removed from the solid media and dissolution experiments were conducted to determine the amounts of Hg(II) released to water. After pure $Hg(0)_l$ was covered by the clean composite soil for 10 days, the Hg(II) released was 14 times greater than from a pure bead not exposed to a solid. Similar results were obtained when $Hg(0)_l$ was added to the soil composite that was held in a nitrogen filled anaerobic glove bag prior to the incubation to remove oxygen (Fig. 4), suggesting oxygen is not essential for oxidation of the $Hg(0)_l$. The amounts of Hg(II) released from $Hg(0)_l$ beads reacted with the soil composite for 10, 30 and 157 days, were similar to the Hg(II) released from the $Hg(0)_l$ beads removed from the contaminated Y-12 soils.

Reaction of manganese oxides ($MnO_2$ and $Mn_2O_3$) with pure $Hg(0)_l$ beads enhanced Hg(II) release into water by amounts similar to or greater than observed for $Hg(0)_l$ recovered

from contaminated Y-12 soil (Fig 4). Eight day reactions of $Hg(0)_l$ with $MnO_2$ resulted in the same order of magnitude increased release of Hg(II) as the in-situ $Hg(0)_l$ beads. Reaction of $Hg(0)_l$ beads with $Mn_2O_3$ for 10 and 120 days significantly increased Hg(II) releases into water, at concentrations of 89 and 741 times greater than for pure $Hg(0)_l$ beads, respectively. An increase in soluble Hg(II) in water was also found when $Hg(0)_l$ was reacted with sand, kaolinite and $Fe_2O_3$; but these increases, were only 2-3 fold greater than for pure $Hg(0)_l$ and less than either the in-situ $Hg(0)_l$ beads or the Mn oxide treated $Hg(0)_l$ beads. We hypothesize that minor amounts of impurities (e.g., Mn oxides) in the sand, $Fe_2O_3$ and other solids, account for the surface oxidation of $Hg(0)_l$ beads that leads to Hg(II) dissolution in water. It is also possible that these silica sand related solid have the ability to oxidize $Hg(0)_l$ but this oxidation is much less than observed with Mn minerals. It is also less than observed with soils so it is unlikely that these sand related solids are significantly influencing the oxidation of $Hg(0)_l$ under natural condition.

In a recent study, the conversion rate of Hg(0) incubated in Amazon soils to Hg(II) was determined to be 36-88% by thermal desorption analysis, and was correlated to the presence of Mn.[47] It was hypothesized that Mn is one of the major species responsible for the Hg-oxidation process but that more detailed studies are required to clarify this effect.[47] At another gold mining site in South America, known for spills of Hg(0), the only form of Hg found based on thermal desorption analysis was Hg(II) and was also correlated to the presence of Mn.[48] Mn(IV) and Mn(III) oxides are capable of oxidizing metal ions including arsenic (III), cobalt (II), uranium (IV) and chromium (III) in water,[18-27] but redox interactions with $Hg(0)_l$ in soils have not been reported. In natural systems, Mn oxides exist in +2, +3, and +4 oxidation states, and are ubiquitous in soils and sediments worldwide[24]. Reported Mn oxide concentrations in soil on the

Oak Ridge Reservation, where we collected $Hg(0)_l$ contaminated soils for our study, were up to 0.8% by weight.[28]

Since most soils contain some moisture, we also examined the potential involvement of free water in the oxidation of $Hg(0)_l$ by Mn oxides. Coated $Hg(0)_l$ beads were prepared using air dried $Mn_2O_3$, which likely contained trace amounts of free water, and also with $Mn_2O_3$ that had been oven dried at 105°C and held in a $N_2$ flushed glove bag containing a desiccant. The amounts of Hg(II) released in water after 10-day treatments from the two procedures were similar (Fig. 4) and suggests that the presence of free water may not control the oxidized coatings on the $Hg(0)_l$ beads. The oven drying of the $Mn_2O_3$ is not expected to remove all mineral bound water, so the possibility of bound water in facilitating the oxidation of $Hg(0)_l$ needs to be further studied.

The mechanism controlling the solid phase oxidation of $Hg(0)_l$ is not completely understood. In other studies that have examined Hg(0) oxidation under aqueous conditions [18, 29-31], the oxidation of dissolved gaseous Hg is slow unless a liquid Hg(0) metal droplet is present[18]. The oxidation rate increases in the presence of ligands such as chloride or thiols and the reaction appears to occur at the surface of the $Hg(0)_l$ bead [18, 29]. Increasing the oxygen concentration in the solution resulted in an increase in Hg(0) oxidation, suggesting that oxygen is required for this aqueous reaction [18]. In our solid phase oxidation experiments, no change in the subsequent release of Hg(II) was found, irrespective of whether the treatment was performed in a $N_2$ or $O_2$ atmosphere. However, $Hg(0)_l$ oxidation by dissolved oxygen was observed in the presence of sediment and water [31]. In that study, because the oxidation at the surface of $Hg(0)_l$ was not specifically examined – in the presence of water and sediment, it cannot be determined if the $Hg(0)_l$ or dissolved Hg(0) was oxidized in the experiments.

The oxidation of Hg(0) in the gas phase has been extensively studied, since this process is used to create Hg(II) in the flue gases of coal fired power plants to reduce atmospheric Hg emissions[32]. Mn oxides have been examined as catalysts for Hg(0) oxidation in the gas phase[33-35]. In this process, the Mn oxide reacts with HCl in the flue gas and the activated chlorine species acts as the oxidant for the Hg(0)[36]. Oxidation of Hg(0) in the atmosphere[37] and in surface waters is believed to be primarily photochemically driven [38-39] and therefore is quite different from our study, where the solid phase reaction of Hg(0) occurred in dark soils with limited exposure to light.

Although Mn oxides have been shown to oxidize metal ions such as arsenic, cobalt, uranium and chromium[19-27] in solution, oxidation of liquid $Hg(0)_l$ in soils by Mn oxides has not been reported. For other metals the oxidation occurs under aqueous conditions and the water is an important component in the reaction. The reaction of $Hg(0)_l$ we observed with solid mineral phases did not involve free water, and the involvement of water is only through the trace amounts bound to the mineral surfaces. In the absence of detailed study we could only speculate that oxidation of $Hg(0)_l$ may be initiated by the formation of an amalgam between Hg and Mn[40] followed by $Hg(0)_l$ reduction of $Mn^{2+}$ species (this is used to analyze Mn by mercury hanging-drop electrodes)[41]. The formation of Hg amalgam in soil, followed by electron transfer from Hg(0) to Mn(III/IV), is a feasible mechanism for the formation of the HgO coatings in soils. Additional work is required to understand the mechanism of $Hg(0)_l$ oxidation in soils.

**Environmental Implications**

Our studies aimed to understand how $Hg(0)_l$ beads are transformed in ambient soils and mineral assemblages, by investigating the solid phase oxidation of $Hg(0)_l$ and is the first to observe the formation of HgO crystals on the surface of Hg(0) bead. Biester and coauthors[42] noted that Hg species in soils surrounding a mercury mine were released from the soil at temperatures expected for the release of HgO. They inferred that HgO formed during heating of Hg-containing ores to recover Hg from the mined material based on the assumption that the HgO only formed at temperatures between 300-350$^oC$. Similarly, asymmetric particles of Hg were found after soil containing $Hg(0)_l$ from a chlor-alkali plant was thermally treated at 220$^oC$[43] and it was suggested that HgO or $HgSO_4$ formed due to the thermal treatment. In our study, the $Hg(0)_l$ beads have been in contact with the soil for decades following their spills at the site. The HgO crystallites present on these beads would have been formed at ambient temperature, because the elevated temperatures noted by others, did not exist in surface soils. The presence of HgO in $Hg(0)_l$ contaminated soils indicates that the formation of HgO as patchy crystals or coatings on $Hg(0)_l$ beads likely occurs at $Hg(0)_l$ contaminated sites worldwide.

The formation of HgO on $Hg(0)_l$ could increase Hg mobility since HgO, with a solubility of $10^{-3.6}$ M [44, 45], is 3 orders of magnitude more soluble than Hg(0) and has a high rate of dissolution (~$10^{-9}$ mol $cm^{-2}s^{-1}$) [44]. The observation of HgO crystallites on $Hg(0)_l$ does not imply that HgO will be a dominate form of mercury at sites contaminated with $Hg(0)_l$. As HgO dissolves in water, Hg(II) would form strong complexes with reduced sulfur, organic matter, and surface functional groups of minerals such as iron oxyhydroxides and Mn oxides.[3,4,7-9, 12, 46-48] It is thus expected that the HgO formed at the surface of the $Hg(0)_l$ will continue to change, and the lifespan of HgO in soil will depend on the hydrologic conditions in the soil. Whereas the porewater movement will control the solubilization and mobility of the HgO at the bead surface,

315 the composition of the surrounding soils will determine the types of Hg(II) complexes and
316 persistence of Hg in soils. Transformation of the HgO is expected to occur in ground and/or
317 surface waters, since HgO is thermodynamically unstable under most environmental conditions,
318 and the kinetics of the transformation requires further investigation.

319 A recent study of 3000 mercury contaminated sites worldwide estimated Hg release at a
320 rate of 116 Mg $yr^{-1}$ from contaminated sites into the hydrosphere. Chlor-alkali facilities, with
321 over 150 active and inactive sites identified globally, have historic contamination of $Hg(0)_l$ in
322 soils and sediments, and more than 40% of these facilities are estimated to be located adjacent to
323 coastal or riverine systems[1]. At the Y-12 complex in Oak Ridge, TN it is estimated that
324 approximately 193,000 kg of Hg was lost to the environment and ~6.7 kg Hg leaves the site
325 annually via surface water discharges alone and the Hg is primarily in the form of dissolved
326 oxidized Hg(II).[16] The flux of dissolved Hg(II) is likely impacted by the HgO coating we observe
327 on the ubiquitous $Hg(0)_l$ found at the site. Rainfall, water flow, and HgO dissolution processes in
328 combination would influence Hg(II) transport in water. High concentrations of Hg(II) have also
329 been observed in streams associated with artisanal gold mining operations that use $Hg(0)_l$. At a
330 site in Indonesia, where highly contaminated Hg wastes were disposed of, total Hg was detected
331 in surface water at concentrations as high as 9.1 ug/L and 95% was determined to be Hg(II)[46].
332 The increased mobility of Hg associated with the formation of oxidized Hg coatings will be
333 especially important in environments where hydrologic cycles create conditions for the
334 formation of HgO during dry periods and mobilization during wet periods.

335 $Hg(0)_l$ contaminated sites resulting from artisanal gold mining and industrial processes
336 are present as long term sources of Hg to the environment.[1] Our study shows that the formation
337 and dissolution of HgO coatings have the potential for enhanced migration of Hg(II). Our

laboratory study indicates that up to 700 times more Hg(II) may be released from Hg beads with coating than without. Thus this potentially important phenomenon needs to be considered when assessing the long-term fate of mercury at these sites. The rate at which Hg distributes through the water environment may be greatly underestimated if the formation of soluble HgO coatings is not taken into consideration.

## Author Contributions

C.L.M. and D.B.W contributed equally to this work.

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## Supporting Information Available

This information is available free of charge via the Internet at http://pubs.acs.org

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494
495 **Figure Captions**

496 Figure 1: Photographs of mercury beads in (a) soil collected from the mercury spill site at the Y-
497 12 facility in Oak Ridge, TN; (b) uncoated bead of $Hg(0)_l$; (c, d) coated Hg(0) beads after
498 reacting with soil in the laboratory. (e) SEM image of a $Hg(0)_l$ bead protruding from a crack in
499 the soil (a), showing a distinct solid phase coating which is likely HgO.

500

501 Figure 2: (a) SEM images of a mercury bead isolated from contaminated soil (see Fig. 1a)
502 showing distinct Hg associated crystals and clay particles, and (b) a higher resolution image of
503 Hg-containing crystals on the surface of the mercury bead. (c) SEM image and (d) energy
504 dispersive x-ray spectra of pure $Hg(0)_l$ (magenta) and a crystal on the surface of the bead (black).
505 The presence of both oxygen (~0.5 kev) and Hg (~2.2 kev) in the crystal, compared with only Hg
506 with no oxygen in the $Hg(0)_l$ indicates that the orthorhombic crystal resembles the typical HgO
507 mineral montroydite.

508

509 Figure 3: Mercury release over time from beads of $Hg(0)_l$ placed in deionized water: open
510 symbols are measurements of the dissolved $Hg(0)_g$ and filled symbols are the oxidized Hg(II) in
511 water. Although dissolved $Hg(0)_g$ followed a similar trend, $Hg(0)_l$ beads removed from soil
512 (Figure 1a) released a greater amount of oxidized mercury (blue) than did a pure bead (red).
513 The data for the soil Hg beads are presented as the average and standard deviation of the two
514 beads.

515

516 Figure 4: Oxidized Hg(II) released into water from both treated and untreated $Hg(0)_l$ beads
517 measured over time following addition of the water. Bead treatments are summarized in Table 1.

Error bars represent standard deviation of multiple replicate experiments. $Hg(0)_l$ reaction time with the solid phase is given for each treatment. The pure bead was not reacted with any solid phase so no reaction time is noted. The reaction time of the $Hg(0)_l$ in the in-situ soil sample is not known. The major spills of $Hg(0)_l$ at the Y-12 facility occurred between 1950-1953 so this $Hg(0)_l$ has likely been reacting with the soil for decades. All experiments were conducted in air except the one labeled with $N_2$ was conducted in an $N_2$ atmosphere. The samples are grouped as controls (grey), $Hg(0)_l$ collected from soil (red), laboratory reacted $Hg(0)_l$ in a soil composite (green), and $Hg(0)_l$ reacted with manganese oxides (blue), and other solids (yellow).

Table 1: Laboratory treatments used to examine the formation of HgO on $Hg(0)_l$ beads. $Hg(0)_l$ was incubated in air or with a solid phase.

| Treatment | Abbreviation | Solid Phase Description | Reaction time |
|---|---|---|---|
| Pure $Hg(0)_l$ | Pure $Hg(0)_l$ | No solid, $Hg(0)_l$ stored under ambient lab air | 8-10 days |
| In-situ soil | In-Situ | $Hg(0)_l$ removed from a soil core sample collected at the Y-12 facility in Oak Ridge, TN | years |
| Composite soil, air | Comp, air | Soil composite from soil collected from the Y-12 facility that did not contain $Hg(0)_l$. Incubation occurred under ambient lab air. | 10, 30 and 157 days |
| Composite soil, $N_2$ | Comp, $N_2$ | Soil composite from soil collected from the Y-12 facility that did not contain $Hg(0)_l$. The soil was stored in a anaerobic glove bag prior to the experiment and the incubation occurred under $N_2$. | 8 days |
| Manganese (III) oxide | $Mn_2O_3$ | Bixbyite; contains 2.4% hausmannite ($Mn_3O_4$) | 10 and 120 days |
| Manganese (III) oxide; dried | $Mn_2O_3$; dried | Bixbyite; contains 2.4% hausmannite ($Mn_3O_4$), dried at 105 $^0$C and stored in a $N_2$ flushed glove bag containing a dessicant | 10 days |
| Manganese (IV) dioxide | $MnO_2$ | pyrolusite | 8 days |
| Iron oxide | $Fe_2O_3$ | hematite | 8 days |
| Quartz sand | sand | acid washed sand (< 150 μm) | 8 days |
| Kaolinite | clay | KGA-2 (kaolinite) CMS** clay reference material | 10 days |
| Soil control | Soil control | $Hg(0)_l$ and composite soil added to aqueous reaction vessel simultaneously, no solid phase reaction between $Hg(0)_l$ and soil | 0 days |

*The $Hg(0)_l$ used for all experiments were acid washed $Hg(0)_l$, except the in-situ sample which were $Hg(0)_l$ beads removed from *in situ* soils collected at the Y-12 facility

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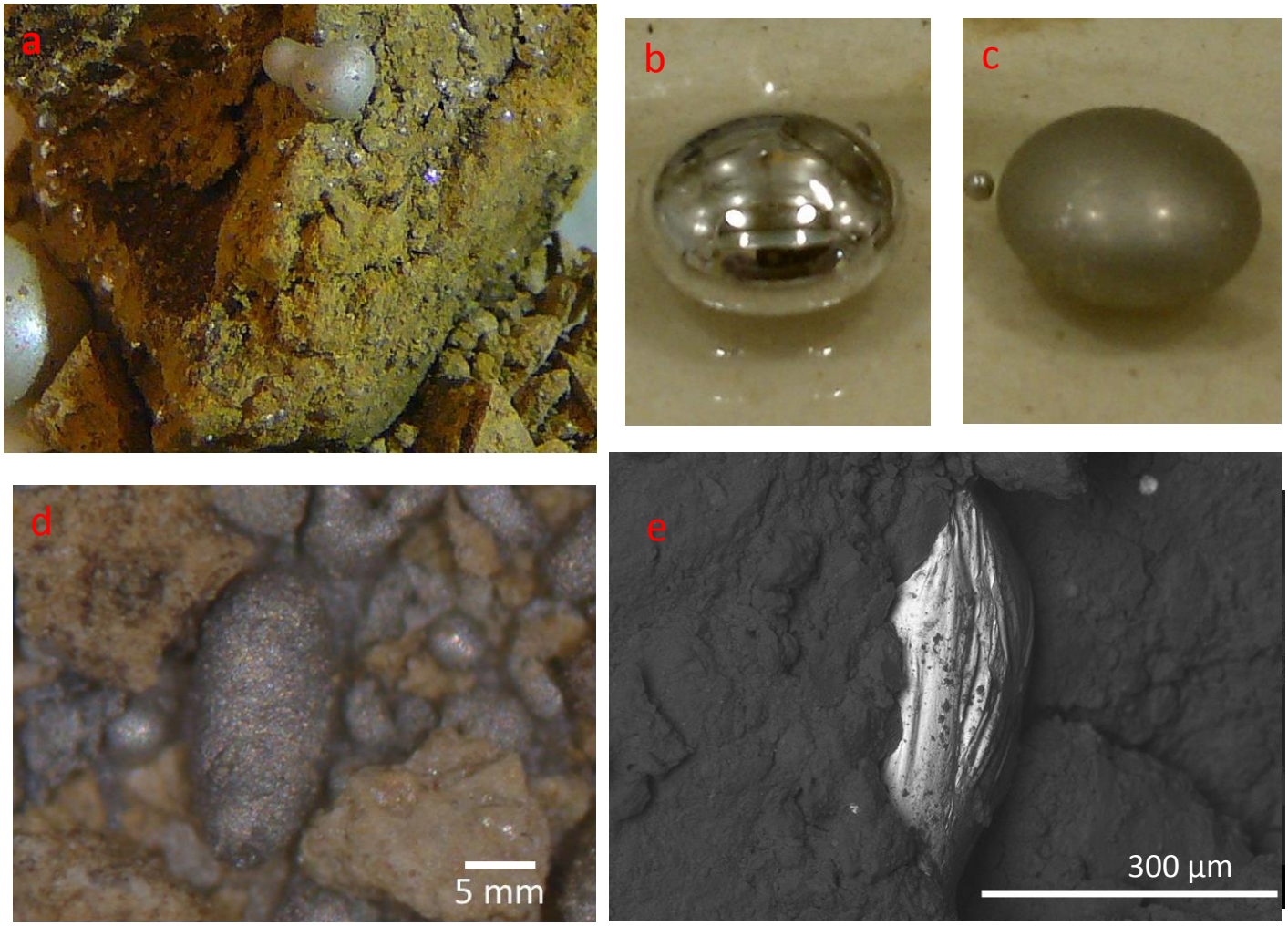
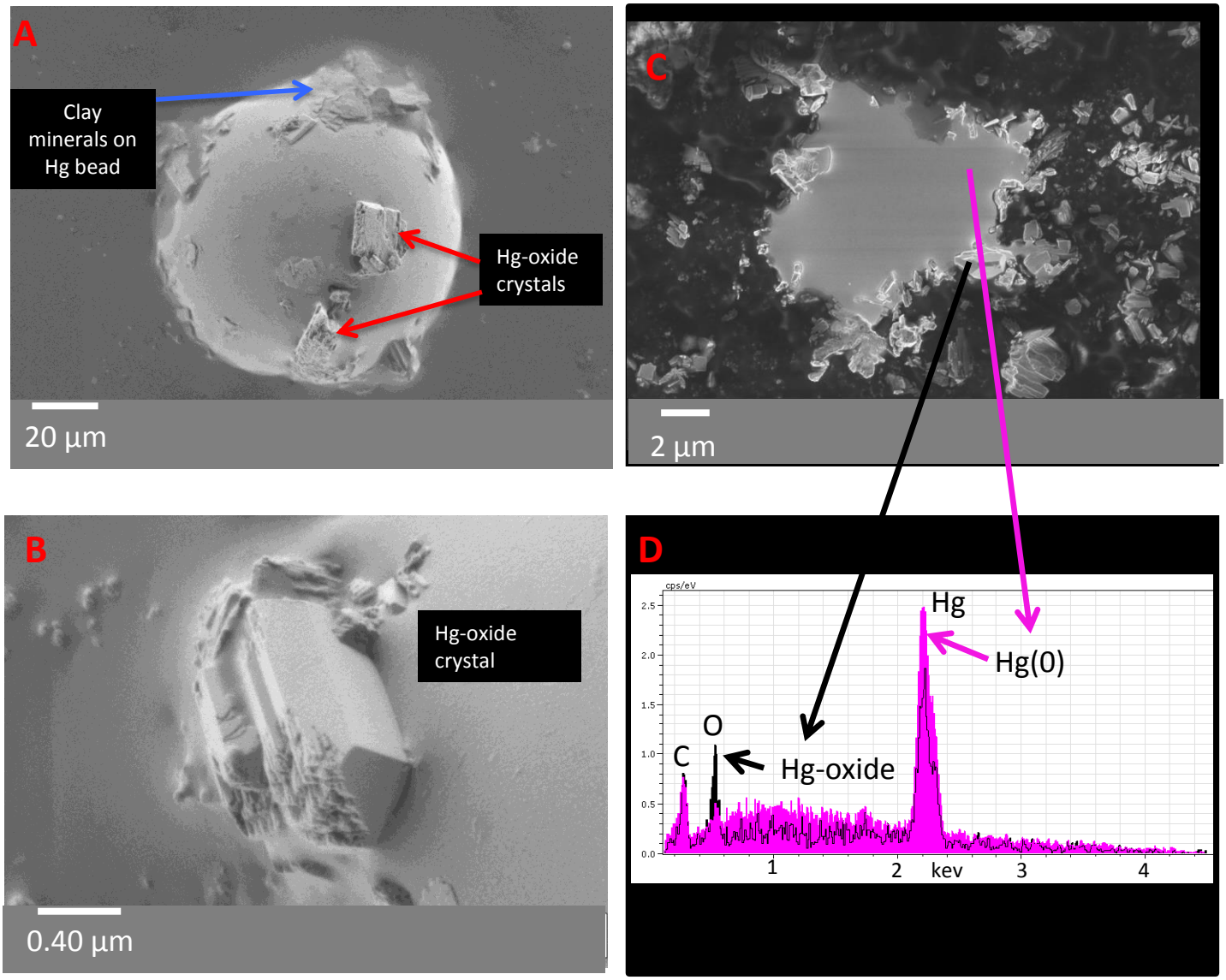
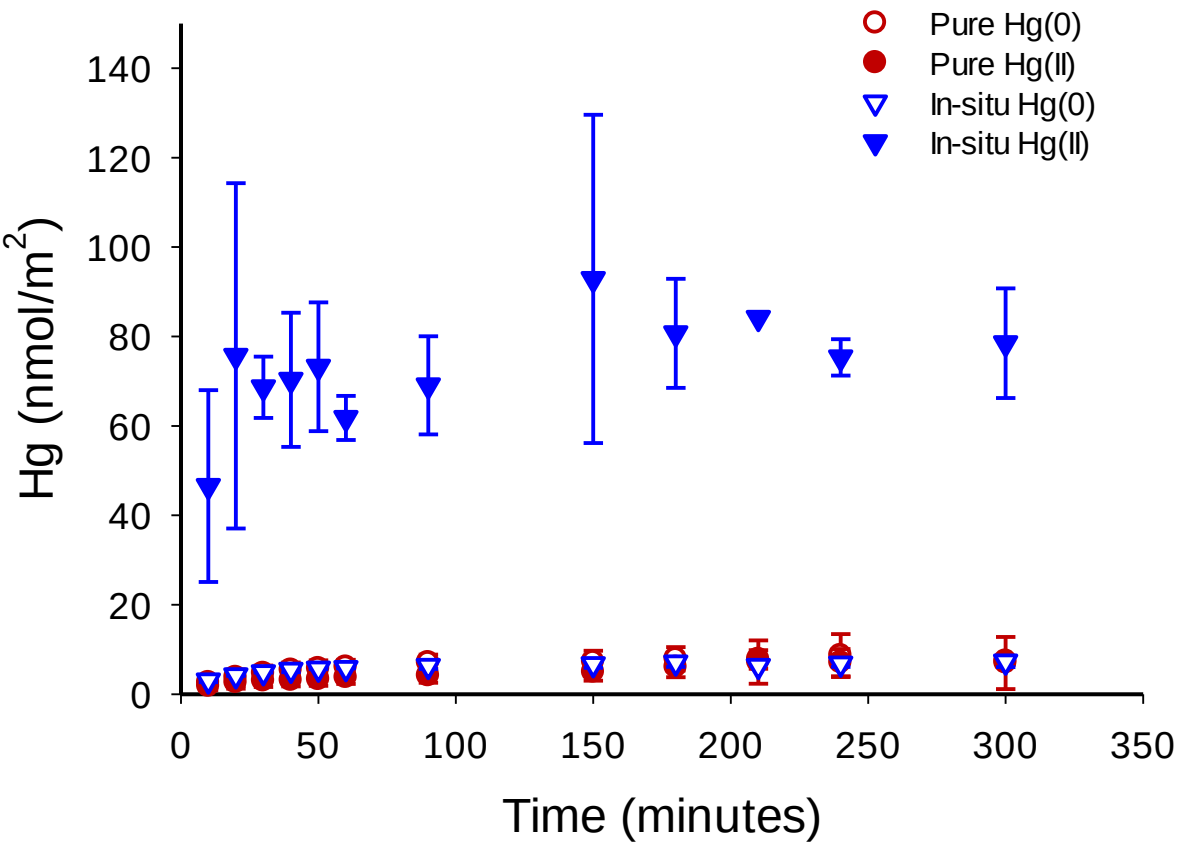

a
b
c
d
5 mm
e
300 µm


A
Clay minerals on Hg bead
Hg-oxide crystals
20 µm
C
2 µm
B
Hg-oxide crystal
0.40 µm
D
cps/eV
Hg
Hg(0)
O
C
Hg-oxide
kev


Pure Hg(0)
Pure Hg(II)
In-situ Hg(0)
In-situ Hg(II)
Hg (nmol/m2)
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300
350
Time (minutes)

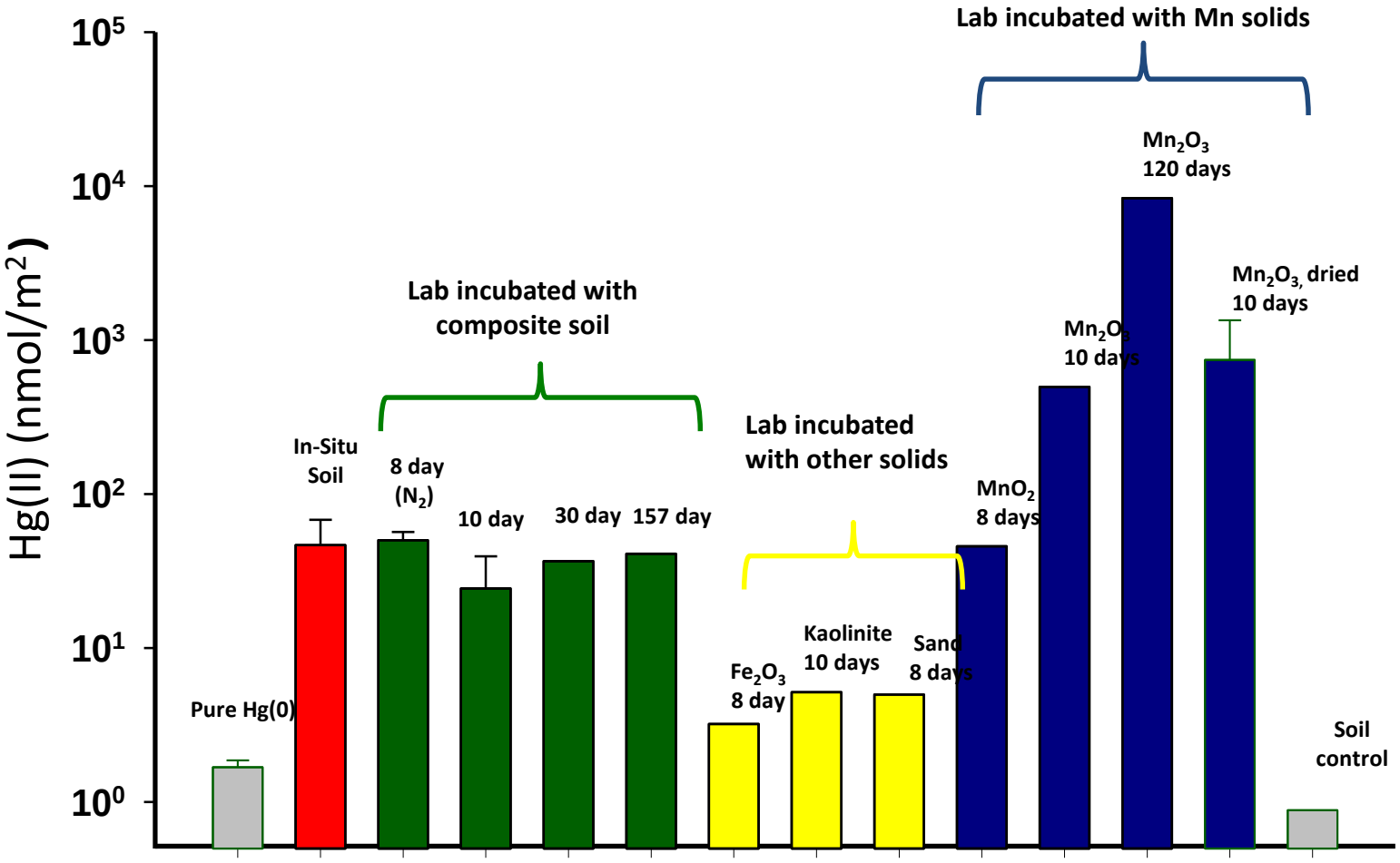
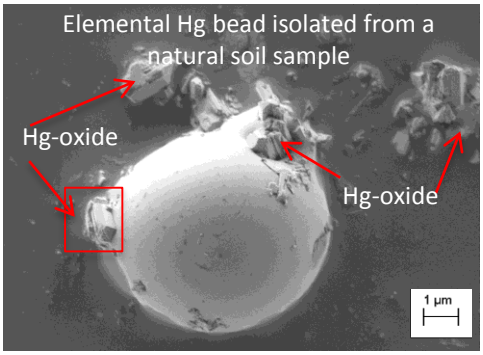

Hg(II) (nmol/m²)
10⁵
10⁴
10³
10²
10¹
10⁰
Lab incubated with Mn solids
Lab incubated with composite soil
Lab incubated with other solids
Pure Hg(0)
In-Situ Soil
8 day (N2)
10 day
30 day
157 day
Fe2O3 8 day
Kaolinite 10 days
Sand 8 days
MnO2 8 days
Mn2O3 10 days
Mn2O3 120 days
Mn2O3, dried 10 days
Soil control

Figure 4

# TOC ART


Elemental Hg bead isolated from a natural soil sample
Hg-oxide
Hg-oxide
1 µm